

We claim:

1. A catalyst system suitable for use in the rearrangement of epoxides to allylic alcohols comprising:
 - (a) at least one primary catalyst comprising at least one homogeneous or heterogeneous, inorganic, organic or complex metal-containing compound
 - (b) at least one activator/modifier comprising at least one phenolic compound, wherein the activator/modifier is present in an amount effective to improve the activity and/or selectivity of the primary catalyst in the rearrangement of a desired epoxide to an allylic alcohol as compared to the use of the primary catalyst without the activator/modifier.
2. The catalyst system according to claim 1 wherein the primary catalyst is selected from among metal oxides, hydroxides, carbonates, carboxylates, and acetylacetones.
3. The catalyst system according to claim 2 wherein the phenolic compound is selected from among phenol, mono- or polysubstituted alkylphenols, nitrophenols, aminophenols, hydroxyphenols, alkoxyphenols, hydroxyacetophenones, salicylic acids and derivatives thereof.
4. The catalyst system of claim 1 wherein the primary catalyst is at least one compound that is inactive in the rearrangement of epoxides in the absence of the activator/modifier.

5. A process for the rearrangement of epoxides comprising:
 - (a) providing a reaction mixture comprising at least one epoxide and a catalyst system, wherein the catalyst system comprises at least one primary catalyst compound and at least one phenolic activator/modifier;
 - (b) reacting at least a portion of the at least one epoxide under conditions effective to rearrange at least a portion of the at least one epoxide into at least one allylic alcohol.
6. The process according to claim 5, wherein the rearrangement of epoxides is carried out at elevated temperature.
7. The process according to claim 6 wherein the rearrangement of epoxides is carried out under reflux.
8. The process according to claim 7 wherein the rearrangement of epoxides is carried out at about 170-250°C.
9. The process according to claim 8 wherein the rearrangement of epoxides is carried out at about 200-230°C.
10. The process according to claim 5, wherein water is removed prior to or in the course of the rearrangement of epoxide.

11. The process according to claim 5, wherein the process is carried out in a batch or continuous mode.
12. The process according to claim 5, wherein the rearrangement of epoxides is carried out at atmospheric or elevated pressure.
13. The process according to claim 5, wherein the amount of primary catalyst is 0.05-10% by weight based on the amount of starting epoxide and the amount of phenolic activator/modifier is 0.025-10% by weight based on the amount of starting epoxide.
14. The process according to claim 5 wherein the reaction mixture further comprises at least one solvent.
15. The process of claim 5, wherein components of the catalyst system are added separately in any sequence to the reaction mixture or are pre-blended.
16. The process according to claim 5 wherein the primary catalyst comprises at least one homogeneous catalyst, which homogeneous catalysts are used in pure form, pre-dissolved in appropriate solvent, or as any commercially available solutions.

17. A process for the preparation of alpha,beta-unsaturated carbonyl compounds comprising:
 - (a) providing a reaction mixture comprising at least one epoxide and a catalyst system;
 - (b) reacting the epoxide under conditions effective to rearrange at least a portion of the epoxides to allylic alcohols; and
 - (c) oxidizing at least a portion of the allylic alcohols by Oppenauer oxidation so as to provide at least one alpha,beta-unsaturated carbonyl compound, wherein the catalyst system comprises at least one primary catalyst and at least one activator/modifier.
18. The process according to claim 17, wherein the rearrangement and the oxidation steps are carried out simultaneously or consequently.
19. The process according to claim 17 wherein the oxidation step includes the addition of at least one hydrogen acceptor
20. The process according to claim 19 wherein the hydrogen acceptor is selected from among cyclohexanone, dihydrocarvone, benzaldehyde, 2-ethylhexanal, furfural.
21. The process according to claim 19, wherein the at least one hydrogen acceptor is added in increments.

- 22. The process according to claim 21 further comprising a periodic removal of alcohol formed from hydrogen acceptor.
- 23. The process according to claim 22, wherein the periodic removal of alcohol is carried out at atmospheric or reduced pressure.
- 24. The process according to claim 19, where the molar ratio between starting epoxide and hydrogen acceptor is about 1:0.7 - 1:1.5.
- 25. The process according to claim 17 further comprising (d) separating the primary catalyst from the reaction mixture.
- 26. The process according to claim 25 wherein the primary catalyst is separated by filtration or distillation and subsequently reused.
- 27. The process according to claim 17, wherein the reaction mixture further comprises at least one solvent.
- 28. The process according to claim 17 wherein the primary catalyst comprises at least one homogeneous catalyst, which homogeneous catalysts are used in pure form, pre-dissolved in appropriate solvent, or as any commercially available solutions.

29. The process according to claim 17 wherein the process is a one-pot process.